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(54) Title: DENTAL IMPRESSION MATERIALS CONTAINING QUADRI-FUNCTIONAL SILOXANE POLYMERS

(57) Abstract

Dental impression materials have improved tear strength and resist tearing upon removal from a set of teeth, especially form a dramatically undercut set of teeth. The dental impression materials incorporate a mono- and quadri-functional (MQ) siloxane component into a silicone-based dental impression material composition. A method of taking a dental impression uses the modified materials.

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DENTAL IMPRESSION MATERIALS CONTAINING QUADRI-FUNCTIONAL SILOXANE POLYMERS

BACKGROUND OF THE INVENTION

The present invention is based upon the discovery that dental impression materials can be produced which have increased tear strength by adding a mono- and 5 quadri-functional siloxane polymer to the material prior to taking a dental impression.

The use of siloxane polymers in dental impression materials has been taught in the prior art. U.S. Patent Nos. 4,657,959 and 4,752,633 disclose dental 10 impression materials which contain silicone polymers having mono- and di-functional silicon atoms. U.S. Patent No. 4,877,854 discloses many polyorganosiloxane polymers useful as dental impression materials. These dental impression materials have suffered from a low 15 tear strength causing problems when removing the molding materials from a set of teeth, particularly teeth having severe undercuts.

The silicone polymers which have been used are based upon linear siloxane chains having functional end 20 groups which enable cross-linking at the chain ends. Little or no cross-linking takes place along the length of the chains.

In order to improved the tear strength of these prior impression materials, various fillers have been 25 added, particularly hydrophobic fillers.

U.S. Patent No. 4,359,565 discloses the use of a diatomaceous earth filler in combination with a polydimethyl siloxane silicone polymer. The polydimethyl siloxanes disclosed container either vinyl 30 end groups or dimethylhydridosilyl end groups. It is known that when impressions are made with siloxane materials, the final product has to date exhibited poor tear strength.

Vinylsiloxane systems have been used for 35 impression materials since they ar odorless, tasteless

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and dimensionally stable. Unfortunately, currently available vinylsiloxane impression materials also exhibit poor tear strength.

A need exists for a vinylsiloxane dental  
5 impression material having improved tear strength and a resistance to tearing upon removal from a set of teeth.

SUMMARY OF THE INVENTION:

The present invention overcomes the problems  
10 encountered by the prior art dental impression materials by providing a dental impression material having improved tear strength and a resistance to tearing upon removal from a set of teeth, especially from a dramatically undercut set of teeth. The present  
15 invention provides a dental impression material having improved tear strength and resistance by incorporating a mono- and quadri-functional (MQ) siloxane component into a silicone-based dental impression material composition. The dental impression materials of the  
20 present invention comprise:

(A) about 25% to about 90% by weight vinyl end-stopped linear siloxane polymer having a viscosity of from about 100 to about 1,500,000 cps at 25°C, or blends of such polymers;

25 (B) a siloxane resin containing mono- and quadri-functional silicon atoms, referred to as an MQ resin, present in an amount of up to about 75 percent by weight such that the total of Components (A) and (B) is from about 15% to about 90% of the total weight of the  
30 dental impression material;

(C) up to about 85% by weight at least one filler selected from the group consisting of silica, cornstarch, quartz, quartz flours, calcium silicate, calcium carbonate, calcium sulfate, pumice flours,

crystoballite flours, hydrated alumina, diatomaceous earth, talc and precipitated and pyrogenically produced silicon dioxide;

5 (D) from about 1 percent to about 10 percent by weight methyl hydrogen polysiloxane cross-linking agent having a viscosity of less than about 500 cps at 25°C;

(E) platinum containing catalyst present in an amount of up to about 6% by weight; and

(F) up to about 4% by weight coloring agent.

10 By incorporating an MQ component in accordance with the present invention, a dental impression material is provided which can cure quickly in a patient's mouth and form a strong and lasting impression of an intraoral structure which remains  
15 intact after removal.

DETAILED DESCRIPTION OF THE INVENTION:

The tear strength of a silicone composition can be increased by adding an MQ component to the composition. It is believed that the quadri-functionality of the MQ 20 resins enables a great deal of cross-linking within a silicone composition. In strictly linear silicone polymers which react only at their end groups, very little cross-linking along the chain takes place. With an MQ polymer, however, a matrix of cross-links is 25 provided which adds to the strength and durability of an entire composition.

The present invention relates to incorporating an MQ-containing siloxane component into a silicone polymer system, and using the system to take a dental 30 impression of an intraoral structure. An intraoral structure is defined herein as a set of teeth, a single tooth, a set of dentures, a set of gums, a prosthetic device, or the like. The materials of the present invention may also be used as bite registration

materials. A bite registration is also herein considered to be included as an impression of an intraoral structure.

According to a preferred embodiment of the present  
5 invention, the dental impression material comprises a siloxane composition having:

(A) about 25% to about 90% by weight vinyl end-stopped linear siloxane polymer having a viscosity of from about 100 to about 1,500,000 cps at 25°C, or  
10 blends of such polymers;

(B) a siloxane resin containing mono- and quadri-functional silicon atoms, present in an amount of up to about 75 percent by weight such that the total of Components (A) and (B) is from about 15% to about 90%  
15 of the total weight of the siloxane composition;

(C) up to about 85% by weight at least one filler selected from the group consisting of silica, cornstarch, quartz, diatomaceous earth, talc and silica gel;

20 (D) from about 1 percent to about 10 percent by weight methyl hydrogen polysiloxane cross-linking agent having a viscosity of less than about 500 cps at 25°C;

(E) platinum containing catalyst present in an amount of up to about 6% by weight; and

25 (F) up to about 4% by weight coloring agent.

Component (A) can generally be described as a siloxane polymer having functional end-stops. In a preferred embodiment, component (A) comprises a vinyl-dimethyl terminated polydimethylsiloxane. Other  
30 polyorganosiloxanes may also be used.

Depending upon what type of dental impression material is desired, the chain length of Component (A) may vary such that a wide variety of viscosities may be employed. For a mono-phasic material from which a  
35 final dental impression is taken in a single step, a

low to medium viscosity impression material is desired. A medium viscosity or "medium body" impression material typically includes a polyorganosiloxane polymer for Component (A) which has a viscosity of from about 100 5 to about 100,000 cps at 25°C. Typical polymers which are readily available on the market include those having viscosities of 100, 200, 1,000, 2,000, 10,000, 60,000, 65,000 and 165,000 cps at 25°C. Any of these may be used for Component (A) of a medium body dental 10 impression material.

Many of the medium body materials may be prepared and applied from a tray or from a syringe. To facilitate application of the heavier viscosity materials, such as those containing a 1,000 to 165,000 15 cps siloxane polymer for Component (A), preparation and application from a tray is preferred.

Thicker viscosity materials are called "tray weight" or "heavy body" materials and typically contain a polyorganosiloxane for Component (A) which has a 20 viscosity of from about 1,000 to about 165,000 cps at 25°C. A viscosity of from about 10,000 to about 100,000 is preferred for component (A) in a heavy body material. Tray weight or heavy body materials are generally not preferred for taking a one-step 25 impression since they provide much less detail than is usually desired.

Tray weight or heavy body materials are commonly used for two-step impression methods. According to a two-step method, a heavy body is used to take a 30 preliminary impression of a tooth, set of teeth, or any portion of dentition. The impression material around the preparation is then relieved (slightly enlarged), e.g. by carving, and filled with a much lighter weight material as described below. The two-layer impression 35 material is then reapplied to the dentition so as to

form a two-layer impression having even greater detail around the preparation.

Putties may also be used for two-step impressions and are preferred in some cases. A putty-weight material may comprise a polyorganosiloxane for Component (A) having a viscosity of from about 100 to about 1,500,000 cps at 25°C. The heavier viscosity polymers are preferably used for Component (A) when formulating a putty-weight material. A putty-weight impression material generally has a much higher filler content than any of the lighter weight materials.

Lighter viscosity compositions are used during the second step of a two-step impression process. These compositions provide the highest detail of the dental impression materials due to their fluidity. These lightweight materials are generally called "syringe weight" and contain very little filler. Syringe weight materials typically contain a polyorganosiloxane for Component (A) which has a viscosity of about 100 to about 65,000 cps at 25°C. Syringe weight materials containing Component (A) having a viscosity of up to 65,000 cps at 25°C may be used but are not preferred. According to some preferred embodiments, the syringe weight material comprises Component (A) having a viscosity of 100 to 10,000 cps at 25°C.

The viscosity of any of the different weight compositions can be controlled by varying the viscosity of the silicone oil, the ratio of silicone oil to filler, the affinity of the filler for the silicone oil (oil absorption number) and the density and specific surface area of the filler.

As can be seen, the amounts and viscosities of Component (A) may vary depending upon the desired application of the dental impression material. In general, the lower viscosity of the polymer used, the

higher the durometer of the cured material. Dental materials containing two or more polymers having different viscosities from each other may also be employed for Component (A).

5       The improved tear strength and tear resistance of the dental impression materials of the present invention can be attributed to the incorporation of Component (B), a siloxane resin containing mono- and quadri-functional silicon atoms. These silicon atoms  
10 are considered mono- and quadri-functional based on the degree of functionality of methylsilicon or other organic substituent subunits. When clusters of quadri-functional silicon atoms are very small, almost all of the silicons are on the outer surface and thus have  
15 unattached SiOH groups sticking out. When these SiOH groups are capped off with Me<sub>2</sub>Si - or M units, an MQ resin results.

At the lower molecular weight end of MQ resins are tetrakis(trimethylsiloxy)silane, (Me<sub>3</sub>SiO) or M<sub>4</sub>O, and  
20 tris(trimethylsiloxy)silanol, (Me<sub>3</sub>SiO)<sub>3</sub>SiOH or M<sub>3</sub>O<sup>OH</sup>. At the upper end of the weight range are gels. The most useful materials are those with a molecular weight range of from about 1,000 to about 10,000. A broader range of materials may also be used, for instance,  
25 materials in the molecular weight range of about 100 to about 100,000. The range of MW in the product, or polydispersity, is usually broad and somewhat dependent upon the method of preparation.

Based upon the total weight of the impression  
30 material, Component (B) may be present in an amount of up to about 75 parts by weight. Preferably, Component (B) is present in an amount of from about 1 to about 25 percent by weight, more preferably from about 5 to about 15 percent by weight. In a particularly  
35 preferred embodiment, Component (B) is present from

about 5 to about 7 percent by weight. Component (B) preferably has a viscosity of from about 4,000 to about 6,000 cps at 25°C.

The combination of Components (A) and (B) should  
5 make up from about 15 to about 90 percent by weight of  
the total impression material formulation.

Component (C) is a filler which may be added to  
the dental impression material in an appropriate amount  
depending upon the viscosity desired. As discussed  
10 above with respect to Component (A), very little filler  
is added to provide a syringe weight material whereas  
a large amount of filler is added to provide a putty-  
weight material. Generally, the filler is added in  
amounts of up to about 85 percent by weight based upon  
15 the total weight of the material. For a syringe weight  
material, between about 5 and about 35 percent by  
weight Component (C) are added. For a putty-weight  
material, about 55 to about 85 percent by weight  
Component (C) is added. The amount of filler and the  
20 viscosity of Component (A) may be varied within their  
appropriate ranges to provide the various weight dental  
impression materials discussed herein.

The filler is generally selected from silica,  
silica gel, cornstarch, quartz, quartz flours, calcium  
25 silicate, calcium carbonate, calcium sulfate, pumice  
flours, crystoballite flours, hydrated alumina,  
diatomaceous earth, talc and precipitated and  
pyrogenically produced silicon dioxide and other  
fillers known to those of ordinary skill in the art.  
30 High surface area fillers, e.g. 100 m<sup>2</sup>/gm and higher,  
are preferred. One specific filler which may be used  
is in many of the compositions is Aerosil™ available  
from Degussa Company, Richfield Park, New Jersey.

Component (D) comprises a cross-linker containing  
35 hydride substituents off of a polysiloxane chain.

Preferred cross-linkers include methyl hydrogen polysiloxanes, preferably linear methyl hydrogen polysiloxanes. The cross-linking agent preferably has a viscosity of less than about 250 cps at 25°C and more 5 preferably from about 25 to about 75 cps at 25°C. Preferably, up to about 50 percent of the substituents off of the siloxane chain are hydride substituents.

Component (D) is preferably present in an amount of between 1 and about 10 percent by weight depending 10 upon the viscosity and the desired degree of cross-linking. Greater amounts of cross-linker are employed with formulations for harder impression materials, e.g. bite registration materials. More preferably, from about 3 to about 8 percent by weight Component (D) is 15 employed. In one embodiment, when about 3 to about 8 percent by weight Component (D) is employed, the cross-linker has a viscosity of about 40 centipoise at 25°C.

Component (E) is a platinum catalyst used to catalyze the cross-linking of the siloxane components 20 within the dental material. In a preferred embodiment, Component (E) is a vinyl-dimethyl terminated polydimethylsiloxane platinum complex. When mixed with the cross-linking agent and reactive polymers and fillers, the platinum catalyst allows the composition 25 to cure relatively quickly such that the dental impression material does not need to remain within a patient's mouth for any extended period of time.

Since the platinum catalyst in the presence of cross-linker and reactive polymer and/or filler allows 30 the composition to cure so quickly, it is separated from the cross-linking agent such that the dental impression material comprises two individual phases which are mixed just prior to use. The one phase contains the platinum catalyst while the other phase 35 contains the cross-linking agent. Preferably,

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Components (A) and (C) are divided among the two phases such that the viscosities of the two phases are substantially similar. Component (B) is added to a first phase which contains the cross-linker whereas the 5 platinum catalyst is incorporated into the second phase.

Component (E) is preferably present in an amount of up to about 6 percent by weight depending upon the available vinyl reactive units in components (A) and 10 (B). The more vinyl present in the uncured material, the more catalyst and cross-linker necessary. In a preferred embodiment, the platinum catalyst is added such that approximately 20 ppm of platinum is available in the material. The platinum catalyst is preferably 15 a platinum complex containing vinyl-dimethyl terminated polydimethylsiloxane and platinum supplied from a platinum tetrachloride salt.

Component (F) is a coloring agent which facilitates inspection of the detail provided by the 20 impression material. The coloring agent is preferably present in an amount of up to about 4 percent by weight, about 0.2 to about 4 percent being a more preferred range. Typical coloring agents used for Component (F) include FDC colors and iron oxides.

25 In order to substantially equalize the viscosities between the two phases, usually more filler is added to the phase containing the cross-linking agent than to the phase containing the platinum catalyst. This is especially useful when the cross-linking agent has a 30 low viscosity e.g., about 40 centipoise at 25°C. The increased amount of filler in the phase containing the low viscosity cross-linking agent tends to increase the viscosity of the phase. It is preferred to have substantially equal viscosities between the two phases 35 in order to facilitate miscibility when mixed just

prior to being applied on a patient's teeth. Most preferably, the two phases have identical viscosities.

Preferably, the two phases of a syringe weight material each have a viscosity in the range of from 5 about 1 to about 125,000 cps at 25°C. For medium and heavy weight materials, the viscosities for each phase are preferably from about 75,000 to about 250,000 and about 200,000 to about 800,000 cps at 25°C, respectively. Putty weight materials preferably have 10 viscosities in the range of from about 750,000 to about 1,500,000 cps at 25°C. Of course, it is preferred that the two phases of any weight material have similar, if not almost identical, viscosities.

Although the present invention has been described 15 in connection with preferred embodiments, it will be appreciated by those skilled in the art that additions, modifications, substitutions and deletions not specifically described may be made without departing from the spirit and scope of the invention defined in 20 the appended claims.

WHAT IS CLAIMED IS:

1        1. A dental impression material comprising a  
2 first siloxane composition molded into an impression of  
3 an intraoral structure, said first siloxane composition  
4 comprising:

5              (A) about 25% to about 90% by weight vinyl end-  
6 stopped linear siloxane polymer having a viscosity of  
7 from about 100 to about 1,500,000 cps at 25°C, or  
8 blends of such polymers;

9              (B) a siloxane resin containing mono- and quadri-  
10 functional silicon atoms and having a molecular weight  
11 of from about 100 to about 100,000, said resin present  
12 in an amount of up to about 75 percent by weight such  
13 that the total of Components (A) and (B) is from about  
14 15% to about 90% of the total weight of the dental  
15 impression material;

16              (C) up to about 85% by weight at least one filler  
17 selected from the group consisting of silica,  
18 cornstarch, quartz, quartz flours, calcium silicate,  
19 calcium carbonate, calcium sulfate, pumice flours,  
20 crystoballite flours, hydrated alumina, diatomaceous  
21 earth, talc and precipitated and pyrogenically produced  
22 silicon dioxide;

23              (D) from about 1 percent to about 10 percent by  
24 weight methyl hydrogen polysiloxane cross-linking agent  
25 having a viscosity of less than about 500 cps at 25°C;

26              (E) platinum containing catalyst present in an  
27 amount of up to about 6% by weight; and

28              (F) up to about 4% by weight coloring agent.

1        2. A dental impression material as defined in  
2 claim 1, wherein Component (B) is present in an amount  
3 of between about 1 and about 25 percent by weight.

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1       3. A dental impression material as defined in  
2 claim 1, wherein Component (B) is present in an amount  
3 of between about 5 and about 15 percent by weight.

1       4. A dental impression material as defined in  
2 claim 1, wherein Component (B) is present in an amount  
3 of between about 5 and about 7 percent by weight.

1       5. A dental impression material as defined in  
2 claim 1, wherein Component (A) has a viscosity of  
3 between about 100 and about 1,000 cps at 25°C.

1       6. A dental impression material as defined in  
2 claim 1, wherein Component (A) has a viscosity of  
3 between about 1,000 and about 10,000 cps at 25°C.

1       7. A dental impression material as defined in  
2 claim 1, wherein Component (A) has a viscosity of  
3 between about 10,000 and about 100,000 cps at 25°C.

1       8. A dental impression material as defined in  
2 claim 1, wherein Component (A) has a viscosity of  
3 between about 100,000 and about 1,500,000 cps at 25°C.

1       9. A dental impression material as defined in  
2 claim 1, wherein Component (A) is a vinyl-dimethyl  
3 terminated polydimethylsiloxane.

1       10. A dental impression material as defined in  
2 claim 1, wherein Component (E) is a vinyl-dimethyl  
3 terminated polydimethylsiloxane platinum complex.

1       11. A dental impression material as defined in  
2 claim 1, wherein Component (F) is at least one FDC  
3 color.

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1        12. A dental impression material as defined in  
2 claim 1, wherein Component (F) is at least one iron  
3 oxide material.

1        13. A dental impression material as defined in  
2 claim 1, further comprising a second siloxane  
3 composition having:

4              (A) about 25% to about 90% by weight vinyl end-  
5 stopped linear siloxane polymer having a viscosity of  
6 from about 100 to about 1,500,000 cps at 25°C, or  
7 blends of such polymers;

8              (B) a siloxane resin containing mono- and quadri-  
9 functional silicon atoms and having a molecular weight  
10 of from about 100 to about 100,000, said resin present  
11 in an amount of up to about 75 percent by weight such  
12 that the total of Components (A) and (B) is from about  
13 15% to about 90% of the total weight of the dental  
14 impression material;

15             (C) up to about 85% by weight at least one filler  
16 selected from the group consisting of silica,  
17 cornstarch, quartz, quartz flours, calcium silicate,  
18 calcium carbonate, calcium sulfate, pumice flours,  
19 crystoballite flours, hydrated alumina, diatomaceous  
20 earth, talc and precipitated and pyrogenically produced  
21 silicon dioxide;

22             (D) from about 1 percent to about 10 percent by  
23 weight methyl hydrogen polysiloxane cross-linking agent  
24 having a viscosity of less than about 500 cps at 25°C;

25             (E) platinum containing catalyst present in an  
26 amount of up to about 6% by weight; and

27             (F) up to about 4% by weight coloring agent,  
28 wherein said second siloxane composition is a  
29 coating on top of said first siloxane composition and  
30 wherein said second siloxane composition has a

31 viscosity which is less than a viscosity of the first  
32 siloxane composition.

1        14. A method of taking a dental impression  
2 comprising:

3            applying a first dental impression material to an  
4 intraoral structure;

5            allowing said first dental impression material to  
6 substantially cure so as to maintain the impression of  
7 said intraoral structure when removed therefrom; and

8            removing said first dental impression material  
9 from said intraoral structure to form a dental  
10 impression, wherein said first dental impression  
11 material comprises:

12            (A) about 25% to about 90% by weight vinyl end-  
13 stopped linear siloxane polymer having a viscosity of  
14 from about 100 to about 1,500,000 cps at 25°C, or  
15 blends of such polymers;

16            (B) a siloxane resin containing mono- and quadri-  
17 functional silicon atoms and having a molecular weight  
18 of from about 100 to about 100,000, said resin present  
19 in an amount of up to about 75 percent by weight such  
20 that the total of Components (A) and (B) is from about  
21 15% to about 90% of the total weight of the dental  
22 impression material;

23            (C) up to about 85% by weight at least one filler  
24 selected from the group consisting of silica,  
25 cornstarch, quartz, quartz flours, calcium silicate,  
26 calcium carbonate, calcium sulfate, pumice flours,  
27 crystoballite flours, hydrated alumina, diatomaceous  
28 earth, talc and precipitated and pyrogenically produced  
29 silicon dioxide;

30            (D) from about 1 percent to about 10 percent by  
31 weight methyl hydrogen polysiloxane cross-linking agent  
32 having a viscosity of less than about 500 cps at 25°C;

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33           (E) platinum containing catalyst present in an  
34 amount of up to about 6% by weight; and  
35           (F) up to about 4% by weight coloring agent.

1           15. A method as defined in claim 14, wherein said  
2 first dental impression material comprises a two-part  
3 system, said two-part system comprising:  
4           part (I) Component (B), Component (D), a portion  
5 of Component (A) and a portion of Component (C); and  
6           part (II) comprises Component (E), and the  
7 remaining portions of Components (A) and (C), wherein  
8 said method includes the step of mixing parts (I) and  
9 (II) to form said first dental impression material  
10 prior to applying said first dental impression material  
11 to said intraoral structure.

1           16. A method as defined in claim 14, wherein said  
2 method further includes the step of applying a second  
3 dental impression material to said dental impression to  
4 from a two-layer dental impression material, said  
5 second dental impression material comprising:

6           (A) about 25% to about 90% by weight vinyl end-  
7 stopped linear siloxane polymer having a viscosity of  
8 from about 100 to about 1,500,000 cps at 25°C, or  
9 blends of such polymers;

10          (B) a siloxane resin containing mono- and quadri-  
11 functional silicon atoms and having a molecular weight  
12 of from about 100 to about 100,000, said resin present  
13 in an amount of up to about 75 percent by weight such  
14 that the total of Components (A) and (B) is from about  
15 15% to about 90% of the total weight of the dental  
16 impression material;

17          (C) up to about 85% by weight at least one filler  
18 selected from the group consisting of silica,  
19 cornstarch, quartz, quartz flours, calcium silicate,

20 calcium carbonate, calcium sulfate, pumice flours,  
21 crystoballite flours, hydrated alumina, diatomaceous  
22 earth, talc and precipitated and pyrogenically produced  
23 silicon dioxide;

24 (D) from about 1 percent to about 10 percent by  
25 weight methyl hydrogen polysiloxane cross-linking agent  
26 having a viscosity of less than about 500 cps at 25°C;

27 (E) platinum containing catalyst present in an  
28 amount of up to about 6% by weight; and

29 (F) up to about 4% by weight coloring agent,  
30 said second dental impression material having a  
31 viscosity which is less than a viscosity of said first  
32 dental impression material;

33 applying the two-layer dental impression material  
34 to said intraoral structure;

35 allowing said second dental impression material of  
36 said two-layer dental impression material to  
37 substantially cure so as to maintain the intraoral  
38 impression when removed from the oral cavity; and

39 removing said two-layer dental impression material  
40 from said intraoral structure to form a two-layer  
41 dental impression.

## AMENDED CLAIMS

[received by the International Bureau on 20 July 1993 (20.07.93);  
original claims 1,13 and 14 amended;  
remaining claims unchanged (5 pages)]

- 1        1. A dental impression material comprising a  
2 first siloxane composition, said dental impression  
3 material being molded into an impression of an  
4 intraoral structure, said first siloxane composition  
5 comprising the reaction product of:
  - 6            (A) about 25% to about 90% by weight vinyl end-  
7 stopped linear siloxane polymer having a viscosity of  
8 from about 100 to about 1,500,000 cps at 25°C, or  
9 blends of such polymers;
  - 10          (B) up to about 75% by weight siloxane resin  
11 containing mono- and quadri-functional silicon atoms  
12 and having a molecular weight of from about 100 to  
13 about 100,000, said resin present in an amount  
14 effective to increase the tear strength of said dental  
15 impression material, wherein the total of Components  
16 (A) and (B) is from about 15% to about 90% of the total  
17 weight of the dental impression material, said siloxane  
18 resin increasing the tear strength of the impression  
19 material by providing a matrix of cross-links enabled  
20 by the quadri-functionality of the resin, wherein the  
21 matrix of cross-links adds to the strength and  
22 durability of the entire composition;
  - 23          (C) up to about 85% by weight at least one filler  
24 selected from the group consisting of silica,  
25 cornstarch, quartz, quartz flours, calcium silicate,  
26 calcium carbonate, calcium sulfate, pumice flours,  
27 cristobalite flours, hydrated alumina, diatomaceous  
28 earth and talc;
  - 29          (D) from about 1 percent to about 10 percent by  
30 weight methyl hydrogen polysiloxane cross-linking agent  
31 having a viscosity of less than about 500 cps at 25°C;
  - 32          (E) a catalytic amount of platinum containing  
33 catalyst; and
  - 34          (F) up to about 4% by weight coloring agent.

1        2. A dental impression material as defined in  
2 claim 1, wherein Component (B) is present in an amount  
3 of between about 1 and about 25 percent by weight.

1        12. A dental impression material as defined in  
2 claim 1, wherein Component (F) is at least one iron  
3 oxide material.

1        13. A dental impression material as defined in  
2 claim 1, further comprising a second siloxane  
3 composition comprising the reaction product of:

4            (A1) about 25% to about 90% by weight vinyl end-  
5 stopped linear siloxane polymer having a viscosity of  
6 from about 100 to about 1,500,000 cps at 25°C, or  
7 blends of such polymers;

8            (B1) up to about 75% by weight siloxane resin  
9 containing mono- and quadri-functional silicon atoms  
10 and having a molecular weight of from about 100 to  
11 about 100,000, said resin present in an amount  
12 effective to increase the tear strength of said dental  
13 impression material, wherein the total of Components  
14 (A1) and (B1) is from about 15% to about 90% of the  
15 total weight of the dental impression material, said  
16 siloxane resin increasing the tear strength of the  
17 impression material by providing a matrix of cross-  
18 links enabled by the quadri-functionality of the resin,  
19 wherein the matrix of cross-links adds to the strength  
20 and durability of the entire composition;

21            (C1) up to about 85% by weight at least one  
22 filler selected from the group consisting of silica,  
23 cornstarch, quartz, quartz flours, calcium silicate,  
24 calcium carbonate, calcium sulfate, pumice flours,  
25 cristobalite flours, hydrated alumina, diatomaceous  
26 earth and talc;

27            (D1) from about 1 percent to about 10 percent by  
28 weight methyl hydrogen polysiloxane cross-linking agent  
29 having a viscosity of less than about 500 cps at 25°C;

30            (E1) a catalytic amount of a platinum containing  
31 catalyst; and

32       (F1) up to about 4% by weight coloring agent,  
33       wherein said second siloxane composition is a  
34       coating on top of said first siloxane composition and  
35       wherein said second siloxane composition has a

36 viscosity which is less than the viscosity of the first  
37 siloxane composition.

1       14. A method of taking a dental impression  
2 comprising:

3       applying a first dental impression material to an  
4 intraoral structure;

5       allowing said first dental impression material to  
6 substantially cure so as to maintain the impression of  
7 said intraoral structure when removed therefrom; and

8       removing said first dental impression material  
9 from said intraoral structure to form a dental  
10 impression, wherein said first dental impression  
11 material comprises:

12       (A) about 25% to about 90% by weight vinyl end-  
13 stopped linear siloxane polymer having a viscosity of  
14 from about 100 to about 1,500,000 cps at 25°C, or  
15 blends of such polymers;

16       (B) a siloxane resin containing mono- and quadri-  
17 functional silicon atoms and having a molecular weight  
18 of from about 100 to about 100,000, said resin present  
19 in an amount of up to about 75 percent by weight such  
20 that the total of Components (A) and (B) is from about  
21 15% to about 90% of the total weight of the dental  
22 impression material;

23       (C) up to about 85% by weight at least one filler  
24 selected from the group consisting of silica,  
25 cornstarch, quartz, quartz flours, calcium silicate,  
26 calcium carbonate, calcium sulfate, pumice flours,  
27 cristobalite flours, hydrated alumina, diatomaceous  
28 earth, talc and precipitated and pyrogenically produced  
29 silicon dioxide;

30       (D) from about 1 percent to about 10 percent by  
31 weight methyl hydrogen polysiloxane cross-linking agent  
32 having a viscosity of less than about 500 cps at 25°C;

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/01930

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : A61K 6/10; A61C 9/00

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/109; 524/862, 861, 734, 745, 788, 791, 789, 786, 588, 47, 442, 425, 423, 444, 437, 448, 451

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,064,891 (FUJIKI ET AL) 12 NOVEMBER 1991. Column 2, line 46-column 3, line 6, Examples 1 and 7, column 3, lines 15-56	1,5,6,9 & 12
Y	US, A, 4,035,453 (HITTMAIR ET AL) 12 JULY 1977. Column 2, line 1-column 4, line 30.	1-13
Y	US, A, 4,609,687 (SCHWABE ET AL) 02 SEPTEMBER 1986. Column 1, line 53-column 2, line 3.	14-16
A	US, A, 4,222,983 (AUGUST ET AL) 16 SEPTEMBER 1980.	1-16
A	US, A, 3,950,300 (HITTMAIR ET AL) 13 APRIL 1976	1-16

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	
"A"	document defining the general state of the art which is not considered to be part of particular relevance
"B"	earlier document published on or after the international filing date
"L"	document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"Z"	document member of the same patent family

Date of the actual completion of the international search

21 APRIL 1993

Date of mailing of the international search report

25 MAY 1993

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**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/US93/01930

**A. CLASSIFICATION OF SUBJECT MATTER:**  
**US CL :**

523/109; 524/862, 861, 734, 745, 788, 791, 789, 786, 588, 47, 442, 425, 423, 444, 437, 448, 451